HYDRODESULFURIZATION OF THIOPHENE ON H- AND NiH-FAUJASITES X AND Y

N.I. JAEGER, R.NOWAK and G. SCHULZ-EKLOFF
Institut für Angewandte und Physikalische Chemie, Forschungsgruppe Angewandte Katalyse, Universität Bremen, D-2800 Bremen 33, FRG

ABSTRACT

In the hydrodesulfurization of thiophene catalyzed by Ni loaded faujasites two active sites seem to be effective. Besides the Brønsted acidic sites the hydrogenolysis activity of the metal phase is essential for maintaining a stable rate of thiophene conversion and for the prevention of coke deposition. The observed particle size distribution suggests a more effective contribution of the small fraction of larger crystallites (d > 4 nm) to the hydrogenation activity of the catalyst.

INTRODUCTION

The most effective hydrodesulfurization catalysts are based on Co/Mo supported on γ-Al_2O_3. The active phases MoS_2 and Co_9S_8 are responsible for hydrogenation and hydrogenolysis respectively in a model of contact synergism proposed by Delmon [1]. The need for two active sites warrants the study of other groups of bifunctional catalysts, namely metal loaded zeolites in the catalytic hydrodesulfurization reaction. In an extensive study of the properties of transition metal loaded zeolites Brooks [2] demonstrated the capability of Ni loaded faujasites in the hydrodesulfurization of thiophene. In the present study the proposed bifunctionality of the metal loaded zeolite [2], i.e. hydrocracking due to the acidity of the zeolite and minimization of coke formation due to the hydrogenolysis activity of the metal, is tested in more detail.

EXPERIMENTAL

Sodium faujasite X (Si/Al = 1.2; crystal size 5-10 µm) and sodium faujasite Y (Si/Al = 2.8; crystal size 2-3 µm) were prepared by hydrothermal crystallization [3,4]. Ni^{2+}-exchange was carried out in $Ni(CH_3COO)_2$ solutions and for the preparation of H-X, Y samples NH_4CH_3COO-solutions were used. The metal contents were determined by atomic absorption spectroscopy. In the case of NH_4^+ the degree of exchange was determined by backtitration of the solution.

Samples (0.5 g) of the crystalline powders were pressed (0.5 GPa), granulated (0.3 - 0.7 mm), dehydrated in argon (100 ml min^{-1}, 693 K, 16 h,heating rate 5K min^{-1}) NH_4 exchanged samples were converted into the H-form of the zeolite under the same conditions. The NiNaX samples were reduced with hydrogen (80 ml min^{-1}, 573 K, 0.1 MPa 25 h). All reactions were carried out in a fluidized bed reactor.

The crystallinity of the dehydrated and reduced samples was checked by their X-ray pattern as well as their capacities for nitrogen physisorption (77 K, 10 KPa). The particle size distributions were determined by transition electron microscopy (EM 10, Zeiss) following the procedure for sample preparation reported by Nagy et al. [5]. From the approximate degree of reduction (α=0.5 [6]) and the size distribution of the metal crystallites the number of Ni surface atoms could be estimated (Fig. 1).

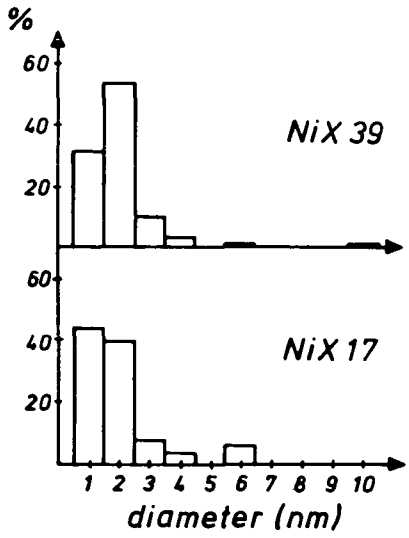

Fig. 1. Particle size distribution for NiX 39 and NiX 17 following reduction of the Ni-exchanged samples

Number and strength of acid sites in the H-X, Y catalysts were determined by titration with n-butylamine solution in the presence of a series of H_0 and H_R indicators [7]. The activities of the samples in the hydrodesulfurization reaction were determined in a fluidized bed reactor (2 ml) containing 0.2 - 0.4 g of the catalyst (60 ml min^{-1}, WHSV: 0.1 h^{-1}, 573 K, 0.1 MPa). The reaction gas mixture consisted of 95 % N_2, 5 % H_2 and 80 vpm thiophene. Thiophene was analyzed by gas chromatography (F 22, Perkin Elmer) using a carbopack column (B-HT-100, Supelco Inc.) and a FID. Hydrocarbons were determined using the same column. The following catalysts were tested: NiX 17, NiX 39 (degree of Ni-exchange 17% and 39% respectively); HX 33 ($H_{27}Na_{57}X$) and HY 100 ($H_{51}Y$).

RESULTS

The distribution of the nickel particle size following reduction is depicted in Figure 1 for the two nickel exchanged zeolites used in the experiments. Table 1 contains the particle size distributions before and after the catalytic reaction (3h time on stream) and an estimation of the number of Ni surface atoms belonging to a selected size range of the Ni particles. Both samples exhibit little sintering. The dispersity of the nickel phase was found to be considerably higher for the NiX 39 sample and only about 25% of the surface atoms belong to crystallites beyond 4 nm in diameter as compared to around 50% in the case of NiX 17.

Table 1

Particle size distribution before and after reaction and related absolute number of Ni surface atoms per gram-unit cell

catalyst	mean diameter nm	following reduction %	following reduction no. of Ni surface atoms per g-u.c.	after 3h time on stream %	after 3h time on stream no. of Ni surface atoms per g-u.c.
NiX 17	1-4	94.3	3.68×10^{23}	89.4	2.17×10^{23}
	5	-	-	2.3	0.37×10^{23}
	6	5.7	2.75×10^{23}	6.1	1.49×10^{23}
	≥ 8	-	-	2.3	1.10×10^{23}
NiX 39	1-4	98.6	11.7×10^{23}	97.4	11.6×10^{23}
	5	-	-	0.5	0.39×10^{23}
	6	0.7	0.88×10^{23}	1.6	1.87×10^{23}
	≥ 8	0.7	2.52×10^{23}	0.5	1.68×10^{23}

The activity of the nickel loaded zeolites are compared in Figure 2 for the first 3 h time on stream. The NiX 39 sample shows a rapid decline in activity starting at high rates of conversion , while NiX 17 starts out at a relatively low value, passes through a maximum and stabilizes at a slightly higher rate of conversion compared to NiX 39. Figure 3 depicts the activities of the hydrogen forms of the faujasites. More than 90% of the acid sites of HY 100 and between 75% - 100% of the acid sites of HX 33 could be titrated. It was found that around 50% of the acidic sites were strong in the case of HY 100 ($pK < -13.3$). In the case of HX 33 around 50% of the acidic sites titrated were of medium strength ($pK > -6.6$). The remaining sites were of lesser acidity. The reactivities of the samples (HY 100 and HX 33) are characterized by rapid deactivation especially in the case of HY 100 having more and stronger acidic sites. Hydrocarbons C_1 - C_4 were formed exclusively in the thiophene conversion.

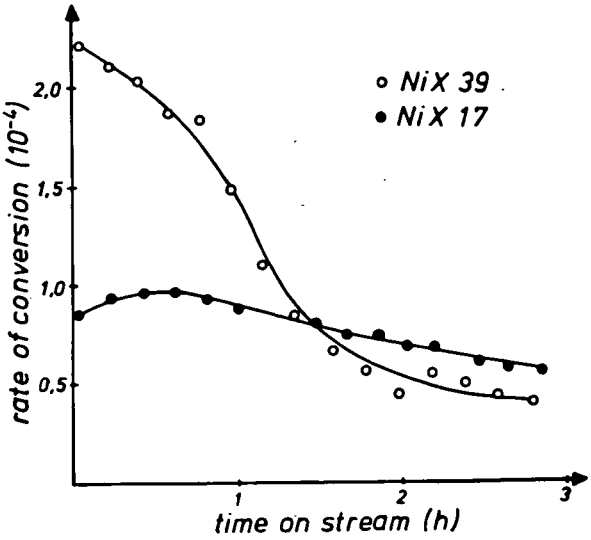

Fig. 2. Rate of conversion (mole thiophene/s·gram-unit cell) vs. time on stream • NiX 17 / o NiX 39

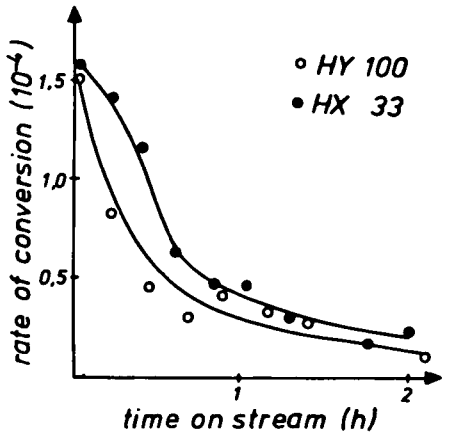

Fig. 3. Rate of conversion (Mole thiophene/s·gram-unit cell) vs. time on stream • HX 33 / o HY 100

DISCUSSION

For thiophene adsorbed on a HY zeolite a strong band was observed in the IR-spectrum, which is due to the S-H vibration. This observation demonstrates the cleavage of the C-S bond, which is assumed to proceed in the presence of Brønsted acidic sites [8]. In the absence of hydrogenolysis activity the high initial activity of the H-X, Y-catalysts decreases rapidly due to coke deposition on strong Brønsted sites.

In the presence of Ni the hydrogenolysis activity of the metal phase may be able to reduce the rate of coke formation on strong acid sites by hydrogenation of coke precursors. The high initial activity of NiX 39 can be attributed to the higher acidity of this zeolite as compared to NiX 17. The activity stabilizes at a value presumably determined by the activity of the metal phase. Both Ni containing catalysts reach about the same stationary level of thiophene hydrodesulfurization.

The estimated number of Ni surface atoms per gram-unit cell is more than twice as large for NiX 39 compared to NiX 17 (Table 1). For metal particles beyond 4 nm in diameter the number is about the same for both catalysts. It is assumed that the larger Ni-crystallites are responsible for the hydrogenation activity of the metal phase in agreement with published results [9,10]. Ni loaded faujasites serve as a model for the study of the bifunctional activity of metal loaded zeolites. Developing the capability of a Ni-faujasite hydrodesulfurization catalyst for the removal of small amounts of thiophene from gases used for synthesis on sulfur sensitive catalysts requires careful consideration of the combined activity of acidic and metal functions.

ACKNOWLEDGEMENT

The authors are grateful to Dr. J. Schweckendiek for the titration of the acid sites.

REFERENCES

1. Hagenbach, G. Courty, Ph., Delmon, B., J. Catal. 31, 264 (1973)
2. Brooks, C.S., Surface Technol. 10, 379 (1980)
3. Charnell, J.F., J. Crystal Growth 8, 291 (1971)
4. Kacirek, H., Lechert, H., J. Phys. Chem. 79, 1589 (1975)
5. Nagy, J.N., Eeno, M. van, Derouane, E.G., J. Catal. 58, 230 (1979)
6. Briese-Gülban, S., Kompa, H., Schrübbers, H., Schulz-Ekloff, G., React. Kinet. Catal. Lett. 20, 7 (1982)
7. Hirschler, E.A., J. Catal. 2, 428 (1963)
8. DeAngelis, B.A., Appierto, G., J. Colloid Interface Sci. 53, 14 (1975)
9. Sauvion, G.N., Djemel, S., Tempere, J.F., Guilleux, M.F., Delafosse, D., in "Catalysis by Zeolites", ed. B. Imelik et al., (Elsevier, Amsterdam 1980), Stud. Surf. Sci. Catal., vol. 5, p. 245
10. Vogt, F., Pitzing, U.-D., Peitzsch, L., Bremer, H., Z. anorg. allg. Chem. 512, 85 (1984)